can show that

the most probable speed is

$$\tilde{v} = \sqrt{\frac{2kT}{m}}$$

the average speed is

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} \simeq 1.13\,\tilde{v}$$

the root mean-square speed is

$$\sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}} = 1.22\,\tilde{v}$$

Equipartition theorem

* this theorem deals with harmonic degrees of freedom

$$H = \sum_{i,j=1}^{\nu} x_i a_{ij} x_j + \tilde{H}$$

$\tilde{H}$ is independent of x_i $i=1,\dots,\nu$

the degrees of freedom x_i $i=1,\dots,\nu$ are harmonic degrees of freedom

$a_{ij} \rightarrow$ positive definite matrix

there may be other (non-harmonic) degrees of freedom

- calculate energy contribution of the quadratic part of the Hamiltonian (10)

$$\left\langle \sum_{ij} x_i a_{ij} x_j \right\rangle = \sum_{ij} a_{ij} \langle x_i x_j \rangle$$

$$\langle x_i x_j \rangle = \frac{\int dx_1 \ldots dx_\nu \, e^{-\beta \sum_{ij=1}^{\nu} x_i a_{ij} x_j} x_i x_j}{\int dx_1 \ldots dx_\nu \, e^{-\beta \sum_{ij=1}^{\nu} x_i a_{ij} x_j}}$$

$$= -\frac{\partial}{\partial(\beta a_{ij})} \int . \int dx_1 . dx_\nu \, e^{-\beta \sum_{ij=1}^{\nu} x_i a_{ij} x_j}$$

$$\int \int dx_1 . dx_\nu \, e^{-\beta \sum_{ij} x_i a_{ij} x_j}$$

diagonalize a_{ij}

$$x_i = \sum_j U_{ij} u_j \quad \rightarrow \quad U^T a U = \Lambda$$

(Λ diagonal

U_{ij} - orthogonal matrix

Jacobian of transformation

$$dx_1 \ldots dx_\nu \rightarrow du_1 \ldots du_\nu$$

is unity

$$\int . \int du_1 . du_\nu \, e^{-\beta \sum_i u_i \Lambda_i u_i} = \prod_{i=1}^{\nu} \left(\frac{\pi}{\beta \Lambda_i} \right)$$

$$\Lambda_i = \sum_{kl} U_{ik}^T a_{kl} U_{li}$$

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$$\langle x_i x_j \rangle = \sum_{kl} U^T_{ik} U_{jl} \langle u_k u_l \rangle$$

$$\langle u_k u_l \rangle = 0 \quad \text{if} \quad k \neq l$$

$$\langle u_k^2 \rangle = \frac{1}{2\beta \lambda_k}$$

$$\langle x_i x_j \rangle = \sum_{kl} U^T_{ik} U_{jl} \frac{1}{2\beta\lambda_k} \delta_{kl} = \frac{1}{2\beta} \sum_k U^T_{ik} \left(\frac{1}{\lambda_k}\right) U_{jk}$$

$$= \frac{1}{2\beta} (a^{-1})_{ij}$$

$$\Downarrow$$

$$\left\langle \sum_{ij} x_i a_{ij} x_j \right\rangle = \cancel{\sum_{ij} kT \sum_k a \ldots} \, a^{-1}_{kj}$$

$$= \frac{kT}{2} \sum_{ij} \sum_k a_{ik} (a^{-1})_{kj} = \frac{kT\nu}{2}$$

* contribution of a harmonic degree of freedom to the average energy: $\boxed{\frac{kT}{2}}$

* contribution of a harmonic degree of freedom to the specific heat: $\boxed{\frac{k}{2}}$

Specific heat of an ideal gas of diatomic molecules in the classical limit (12)

- diatomic molecules translate, rotate, and vibrate (translate means their center of mass moves)

* rotation: $\mathcal{L}_{rot} = \frac{I}{2}\left(\dot\theta^2 + \sin^2\theta\,\dot\varphi^2\right)$

$$= \frac{1}{2I}\left(p_\theta^2 + \sin^2\theta\, p_\varphi^2\right)$$

2-harmonic degrees of freedom (p_θ, p_φ)

* vibration:

$$H = \frac{p_q^2}{2m} + V(q-q_0)$$

$$V(q-q_0) = V(q_0) + \frac{1}{2}V''(q_0)\,q^2$$

(harmonic approximation)

2- harmonic degrees of freedom (p_q, q)

* translation of center of mass

$p_x, p_y, p_z \Rightarrow$ harmonic $\left(\frac{p_x^2+p_y^2+p_z^2}{2M}\right)$

3 - harmonic degrees of freedom

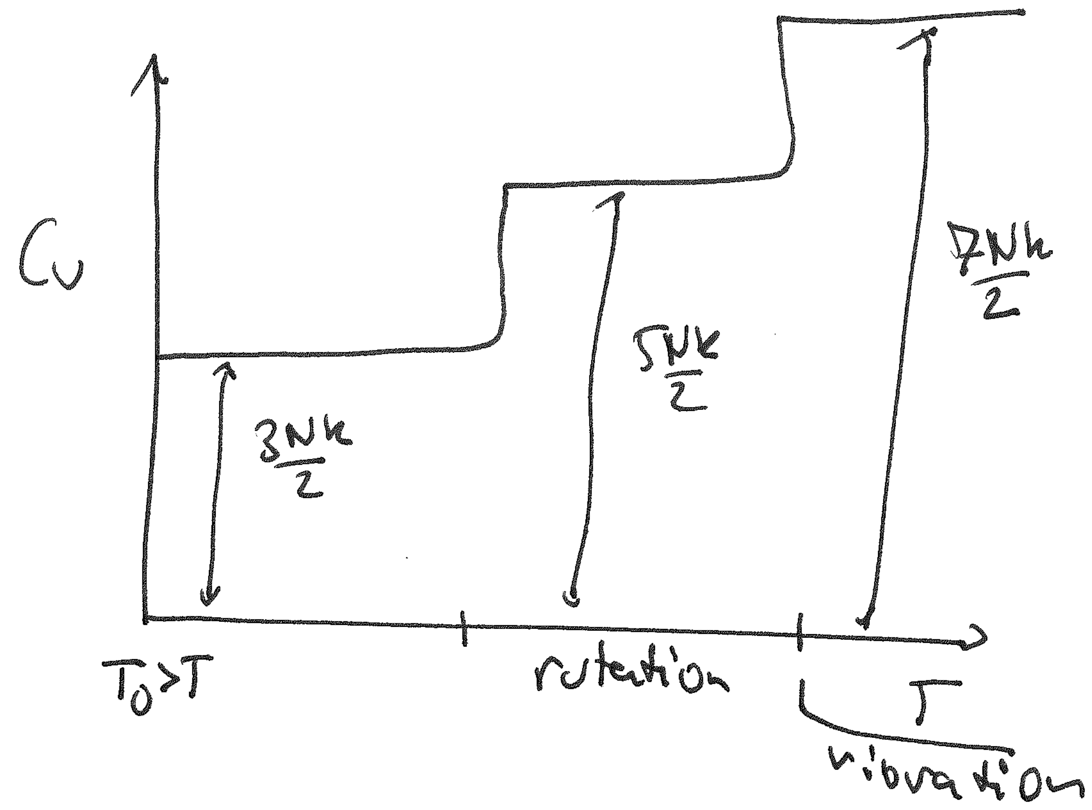
⇓ ⇓ ⇓

expect that specific heat is $\frac{7Nk}{2}$

$$(2+2+3)\frac{Nk}{2}$$

NOT QUITE

- classical limit is reached at different temperatures for translation / rotation / vibration



For an ideal gas of diatomics performing (14)
quantum rotation and vibration, assuming
that they are decoupled, we can proceed
as follows:

* vibration: $H|\psi_n\rangle = E_n|\psi_n\rangle$

$$E_n = \hbar\omega(n + 1/2)$$

contribution to partition function

$$Z_{vib}(T) = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)}$$

$$= e^{-\beta\frac{\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}$$

$$= \frac{e^{-\beta\frac{\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}}$$

* rotation: $H_{rot}|lm\rangle = \frac{\hbar^2}{2I} l(l+1)|lm\rangle$

(rigid rotor)

$$B_{rot} = \frac{\hbar^2}{2I} \quad \text{(rotational constant)}$$

$$Z_{rot}(T) = \sum_{l=0}^{\infty} \underbrace{(2l+1)}_{\substack{\text{degeneracy} \\ m=-l,\dots,l}} e^{-\beta B_{rot} l(l+1)}$$

total partition function: $Z(T) = \frac{1}{N!} Z_{trans}(T)\, Z_{rot}(T)\, Z_{vib}(T)$

can calculate the specific heat in the usual way

(NB: this analysis assumes that translation, rotation and vibration are all decoupled from each other)

From vibrations:

$$C_V = k\left(\frac{T_{vib}}{T}\right)^2 \frac{e^{T_{vib}/T}}{\left(e^{T_{vib}/T}-1\right)^2} \begin{cases} k\,(T_{vib}/T)\, e^{-T_{vib}/T} & \to 0 \text{ as } T \to 0 \\ k & \text{as } T \gg T_{vib} \end{cases}$$

where $T_{vib} = \frac{\hbar \omega_0}{k}$

($C \sim \exp\left(-\frac{\Delta E}{kT}\right)$ (exponential behavior) characteristic of systems with energy gap)

Virial theorem

consider average $\langle x_i \frac{\partial H}{\partial x_j} \rangle$

$x_j, x_i \to$ some degrees of freedom (momenta or positions)

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{\int d\dots dx_j \dots dx \left[x_i \frac{\partial H}{\partial x_j}\right] e^{-\beta H}}{\int d\dots dx_j \dots dx \; e^{-\beta H}}$$

numerator: can be integrated by parts

$$\frac{\partial H}{\partial x_j} e^{-\beta H} = \frac{\partial}{\partial x_j}\left[-\frac{1}{\beta} e^{-\beta H}\right]$$

$$\int dx_j \; x_i \frac{\partial}{\partial x_j}\left[-\frac{1}{\beta} e^{-\beta H}\right]$$

$$= \underbrace{x_i\left[-\frac{1}{\beta} e^{-\beta H}\right]_{x_j^{(-)}}^{x_j^{(+)}}}_{0} - \int dx_j \frac{\partial x_i}{\partial x_j}\left[-\frac{1}{\beta} e^{-\beta H}\right]$$

zero at boundaries $\Rightarrow 0$

$$= \delta_{ij} \; kT \int dx_j \; e^{-\beta H}$$

$$\Downarrow \qquad\qquad \Downarrow$$

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = \delta_{ij} \; kT$$

if $x_i \to$ harmonic one can recover the equipartition theorem

<u>but</u> this theorem is more general

consider a coordinate $\Rightarrow q_i$

$$\langle q_i \frac{\partial H}{\partial q_i} \rangle = kT = \langle q_i \frac{\partial V}{\partial q_i} \rangle = -\langle q_i F_i \rangle$$

$$F = -\frac{\partial V}{\partial q_i} \Rightarrow \text{force on particle}$$

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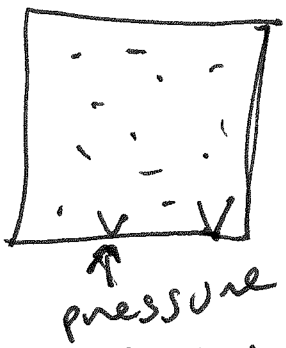
consider an ideal gas



- no force on particles except at boundary

$\Downarrow$

$$-\sum_i \langle \vec{r}_i \cdot \vec{F}_i \rangle = 3NkT$$

force only acts at boundary so we can say $\Rightarrow$

$$-\sum_i \langle \vec{r}_i \cdot \vec{F}_i \rangle = \cancel{\oint (\vec{r}_i \cdot \vec{F}_i) d\vec{\sigma}}$$

~~$\oint d\vec{\sigma}$ integral around boundary~~

$\Downarrow$

$$= + P \oint \vec{r} \cdot d\vec{\sigma}$$

$\oint d\vec{\sigma} \cdot \_ \Rightarrow$ integral around boundary

Gauss' law: $\oint \vec{r} \cdot d\vec{\sigma} = \int (\vec{\nabla} \cdot \vec{r}) dV$

$$= 3V \Rightarrow \boxed{PV = NkT}$$